PREDICTION OF SHORT RANGE MAXIMUM NO_2 CONCENTRATIONS USING SCALAR PDFS

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Abstract

Significant emissions of NO_X (oxides of nitrogen: NO and NO_2) are common from sources such as power stations, road tunnel ventilation outputs and freeways. As these species are chemically reactive ($NO + O_3 \rightarrow O_2 + NO_2$), their concentrations downwind from the source are influenced by both the atmospheric turbulence (dispersion) and the chemical reactions. As part of an ongoing research project to investigate the effects of mixing on chemical reactions in the atmosphere, we make use of a new modelling technique based on the concentration statistics of a non-reactive (conserved) scalar. A simplified form of the model is an upper (conservative) limit on toxic NO_2 concentrations. The novelty of this limit is that it is less conservative than previous methods commonly in use by air quality modellers but has a sound physical basis and can readily be calculated for atmospheric plumes. Model results are presented for NO, O_3 and NO_2. When model predictions for NO_2 are compared to atmospheric field data it is found that the model limit is a conservative bound on their concentrations. The present model is restricted to the plume centreline. The two main inputs are a parameterisation for the concentration fluctuations (conditional dissipation of scalar concentration fluctuations) and the probability density function (pdf) of the conserved scalar in the plume. Careful choices of these inputs are necessary for correct model behaviour and to ensure internal model consistency. Future work needed to improve present model limitations is

described including: use of the pdf transport equation; ways to remove the need for model parameters by appeal to basic physics, and generalisation of the present centreline restriction.

Keywords: turbulence, dispersion, chemical reaction, smog, conditional moment closure, reaction dominated limit.

1. Introduction

Motivation for this work comes from the need to predict concentrations of reactive pollutants in the atmosphere, where effects of turbulent mixing of reactants on chemical reaction can be significant. Since the aim of this work is to understand the fundamental physical processes involved, we consider a simple situation downwind from a point release, such as a power station plume. The only reaction considered is $NO + O_3 \rightarrow NO_2 + O_2$; we ignore the back reaction, which occurs in the presence of sunlight. This reaction is chosen because the adverse health and environmental effects of O_3 and NO_2 are of particular concern.

Various approaches to this problem of the effect of turbulence on chemical reactions in atmospheric flows have been taken in the modelling studies of Vila *et al*. (1990), Galmarini *et al*. (1995), Fraigneau *et al*. (1996), Silue & Mokhtarzadeh-Dehgham (1997), Gonzalez (1997), Ohba *et al*. (1999) and Brown *et al.* (1999). An extension of the present work in a more generalised form is presently being undertaken. Investigation of the scalar dissipation relevant to this particular study is that of Brown & Sawford (2000). The experimental data needed to guide and validate modelling studies are difficult to obtain in the laboratory and even more so in the atmosphere. Information about the effects of turbulent mixing on chemical reactions demands measurements of the fluctuations in reactant concentrations, not just their means. Some observations relevant to the present investigation have been reported in the literature, for example: wind tunnel experiments of Builtjes (1983); the surface layer experiments of Komori *et al*. (1991), Kimura (1980) and Frank *et al*. (1988); and airborne measurements by Janssen *et al*. (1990).

A longer term aim of our work is to obtain predictions of reactive atmospheric pollutants by combining two existing techniques: (1) the conditional moment closure (CMC) theory of Klimenko & Bilger (1999), which was derived for combustion problems, and (2) an

atmospheric scalar probability density function (pdf). CMC predicts reactive scalar concentrations as a function of the statistics of a conserved scalar (conditional reactive scalar statistics). A simple limit of CMC is an upper (conservative) limit on toxic NO_2 concentrations. The novelty of this limit is that it is less conservative than previous methods commonly in use. This limit is known as the reaction dominated limit (RDL) and is obtained by neglecting the effects of micro-mixing (dissipation) in the CMC equations. Such mixing occurs at small scales and acts to bring the reactants into molecular contact where chemical reactions can occur. Neglecting the delay due to micro-mixing effectively assumes that the reactants are brought into contact instantaneously, leading to an over-estimate of the rate at which the chemical reaction proceeds. Thus RDL will always give conservative (upper) estimates for NO_2 concentrations. By including additional modelling for the dissipation term, the RDL limit may be relaxed to give the full CMC model. In this paper the dissipation term is modelled by parameterising the conditional conserved scalar dissipation.

The other technique needed to obtain predictions of reactive atmospheric pollutants is the conserved scalar pdf, $p(x)$, which when integrated between the limits of 0 and x, gives the probability that the conserved scalar is $\leq x$. We choose the clipped-gamma form of Yee & Chan (1997). This pdf is particularly useful for inclusion in CMC modelling of reactive atmospheric species because one of its fundamental assumptions can be used to parameterise the conserved scalar dissipation, which is one of the terms in the CMC equation. This is explained more fully in Section 2. We thus ensure consistency between the chosen pdf and the CMC model. However, this consistency is only on the centreline. Work by Brown & Sawford (2000) presents a method for obtaining the conserved scalar dissipation (needed for the CMC model) from the pdf by the use of the pdf transport equation in a form generalised for the whole plume.

The plan of the paper is as follows: we briefly introduce conserved scalar theory, which is used to derive relationships between reactive scalars such as NO and O_3, and conserved scalars such as NO_X. Next, we give an overview of CMC and explain how to use the pdf of Yee & Chan (1997) in conjunction with CMC. The success of this approach is then demonstrated using limited field data on the NO_X power station plumes from Janssen *et al.* (1990).

2. Model Description

The CMC model is applicable to turbulent reactive flows where mixing of reactants occurs from different streams. The CMC model, itself, is not strongly dependent on the source configuration but the two major inputs to the CMC model, the conserved scalar pdf and the conserved scalar dissipation model, do depend on the source configuration. For the purposes of this present study, we consider experimental data for a plume emitted from the stack of a power generation station, i.e. the source configuration is a point source in a boundary-layer flow.

2.1. Conserved Scalar Theory

The conserved scalar theory of Bilger *et al*. (1991) is useful because it defines the relations between conserved and reactive scalars. Conserved scalars are used to describe the general dispersion of pollutants in the atmosphere, which results from atmospheric turbulence, whereas chemical reactions involve non-conserved scalars.

A conserved scalar (i.e. one not affected by chemical reaction) is often used in dispersion modelling to describe the state of mixing of an atmospheric pollutant with the surrounding ambient fluid in the presence or absence of chemical reaction. In the present case we use total oxides of nitrogen,

$$C_{NO_X} = C_{NO} + C_{NO_2},$$

where C_i is the molar concentration of species *i*. The mixture fraction of this conserved scalar (Bilger *et al*., 1991) is defined as

$$\hat{C} = \frac{C_{NO_X}}{S_{NO}},$$

where S_{NO} is the initial concentration of NO in the plume, and the corresponding concentration of ambient O_3 is S_{O_3}

For simplicity it is assumed here that there is no O_3 present in the initial unmixed NO plume, and no NO present in the ambient O_3 air, although more general conditions can be accounted for in CMC modelling. The range of $\hat{C}$ is between 0 and 1, representing pure ambient fluid and pure plume fluid, respectively. Intermediate values represent proportional mixing of these two fluids.

Bilger *et al*. (1991) have shown, using conserved scalar theory and conservation of mass, that in such simple two-stream mixing, the reactive and conserved scalars are related by

$$\hat{C} = \frac{C_{NO} - C_{O_3} + S_{O_3}}{S_{NO} + S_{O_3}}. \quad (1)$$

When NO from the plume and O_3 from the ambient atmosphere are mixed to the point where they have equal concentrations, they will eventually react completely. Such an equally proportioned mixture is known as a stoichiometric mixture and the corresponding mixture fraction may be obtained from Equation (1) as

$$\hat{C}_s = \frac{S_{O_3}}{S_{NO} + S_{O_3}}.$$

It is sometimes convenient to normalise the mixture fraction, $\hat{C}$, by $\hat{C}_s$ because the latter is representative of the region where most chemical reaction is likely to occur and consequently the region of greatest interest to us.

2.2. Conditional Moment Closure

Klimenko and Bilger (1998) have recently reviewed the theory and use of the CMC technique. Here we give only a brief summary, mainly following the approach of Bilger (1993). We note that the following derivation is not confined to any particular location in the plume, although the model results of CMC presented later are restricted to the centreline because this is where the field data were measured.

The equation for conservation of species is

$$\partial C_i / \partial t + \mathbf{U} \cdot \nabla C_i - \nabla \cdot (\mathrm{D} \nabla C_i) = w_i, \quad (2)$$

where the molecular diffusivity for the scalar, D_i ($\cong 0.2$ cm^2 s^{-1}), is taken as the average of that of the reactants. The reaction rate of species *i* is proportional to the product of the instantaneous concentrations

$$w_{NO} = -kC_{\mathrm{NO}}C_{\mathrm{O_3}},$$

where *k* is the reaction rate constant. Averaging this equation gives

$$\overline{w}_{NO} = -k\left(\overline{C}_{\mathrm{NO}}\overline{C}_{\mathrm{O_3}} + \overline{c_{\mathrm{NO}}c_{\mathrm{O_3}}}\right),$$

where overbars represent time averaging and c_i is the fluctuating component of C_i. The second term on the right-hand side, the reactant covariance, is a negative term of the same order of magnitude as the first term, the product of the means. Klimenko and Bilger (1999) have

shown both from experimental data and theoretically that for moments *conditional* on the value of the conserved scalar $\hat{C}$, the covariance may be neglected. Thus the reaction rate can be written in terms of the product of the conditional means

$$< w_{NO} \mid \eta > \approx -kQ_{\mathrm{NO}}Q_{\mathrm{O_3}} = -kQ_{\mathrm{NO}}(Q_{\mathrm{NO}} - \eta(S_{\mathrm{NO}} + S_{\mathrm{O_3}}) + S_{\mathrm{O_3}}), \quad (3)$$

where

$$Q_i = < C_i \mid \hat{C} = \eta >,$$

and η is a sample space variable for $\hat{C}$. We follow the notation of Bilger (1993) in using angle brackets for conditional averages and overbars for non-conditional averages but note that the averaging process is otherwise the same. Other assumptions made in the present study include stationarity, a constant mean velocity field and neglecting the correlation between fluctuating components of the conditionally averaged reactive scalar and fluctuating components of the velocity. Experimentally this third assumption has been found valid for conditional averaging (but not for time averaging) of reactive scalars in reacting boundary layers and non-lifted jet flames (Bilger 1993). By substituting Equation (3) and conditional mean and fluctuating terms into Equation (2), averaging and making use of the above assumptions, we obtain

$$\frac{\partial Q_{\mathrm{NO}}}{\partial(\mathrm{x/H})} = -\frac{kH}{\overline{U}} Q_{\mathrm{NO}} (Q_{\mathrm{NO}} - \eta(S_{\mathrm{NO}} + S_{\mathrm{O_3}}) + S_{\mathrm{O_3}}) + \frac{H}{2\overline{U}} < \chi \mid \eta > \frac{\partial^2 Q_{\mathrm{NO}}}{\partial \eta^2}, \quad (4)$$

where $\overline{U}$ is the mean velocity, H is the plume height (used here as a length scale), and $< \chi | \eta >$ is the mean dissipation of conserved scalar fluctuations conditional on the conserved scalar itself. Only values of Q_{NO} are obtained from the solution of Equation (4). Values for $Q_{\mathrm{O_3}}$ and $Q_{\mathrm{NO_2}}$ are derived from Q_{NO} using conservation relations, as given in Brown & Bilger (1998). The boundary conditions are

$Q_{\mathrm{NO}} = \eta S_{NO}$ for $x/H = 0$

$Q_{\mathrm{NO}} = 0$ for $\eta = 0$

$Q_{\mathrm{NO}} = S_{NO}$ for $\eta = 1$.

The CMC model requires two major inputs: a model for $< \chi \mid \eta >$ and a model for the pdf of the conserved scalar. The term χ is related to the square of the spatial derivative of the conserved scalar; a fuller discussion of χ in this type of plume can be found in Brown &

Bilger (1998). The pdf of the conserved scalar is also needed to obtain mean values from the CMC predictions of the conditional reactive scalar statistics

$$\overline{C}_i = \int_0^1 Q_i(\eta) P(\eta) d\eta , \tag{5}$$

where $P(\eta)$ is the pdf of η. Klimenko & Bilger (1998) reviewed the use of CMC in reactive flows such as combustion and reacting isothermal flows.

Brown & Bilger (1998) have successfully used the CMC approach for turbulent reacting plumes in smog chamber flows, which had a low mean velocity and large turbulence scale. They used pdfs measured in well-controlled laboratory conditions. However, these pdfs are not available for atmospheric flows.

For the present implementation of the CMC model given in Equation (4), we use the same simple linear relationship for the conditional scalar dissipation as that used by Yee & Chan (1997) to derive their pdf. This ensures consistency between the pdf and the conditional scalar dissipation model, which are related to each other (Sinai & Yakhot, 1989; Sabel'nikov, 1998). From atmospheric plume measurements, Yee & Chan (1997) found that

$$\left\langle \left(\frac{\partial \hat{C}}{\partial t} \right)^2 \mid \eta \right\rangle \approx K\eta ,$$

where K is a constant, which has not yet been thoroughly investigated for atmospheric plumes, and has the dimensions of $[\text{time}]^{-2}$. Using Taylor's frozen turbulence hypothesis to convert temporal gradients to spatial gradients gives

$$< \chi \mid \eta >= \alpha\eta , \tag{6}$$

where

$$\chi = 2D\left(\nabla \hat{C}\right)^2 \quad \text{and} \quad \alpha = 2DK / \overline{U}^2 .$$

The parameter α has dimensions of inverse time and is varied through a range of values that are shown on Figure 2 below. In principle, α may be a function of spatial position but for simplicity in the example considered we set α to a constant value for all x. The special case of $\alpha = 0\ s^{-1}$ is the reaction dominated limit (RDL). The second term on the right hand side of Equation (4) is eliminated in this case and the equation is simplified to a convective-reactive balance, which has an analytical solution given in Brown & Bilger (1998). The RDL represents a consideration of instantaneous mixing (at the stack exit) of the plume with

ambient air for every possible combination of plume gas and air (viz. from η = 0 to η = 1). The reactions then take place as the gases travel downstream, rather than the actual longer mixing process that occurs as the mean velocity carries the plume downstream. It should be noted that the while neglecting the delay due to micro mixing is certainly a conservative assumption, predictions of the RDL from any model include some uncertainty. In the present approach, most of this uncertainty will be due to accuracy of the estimate for the mean of the conserved scalar and its pdf. Based on the available experimental evidence (eg. Bilger 93), it is not expected that the assumptions made in deriving Eq. (4) could result in an under-prediction of NO_2 concentrations for the case where α is set to zero.

Equation (4) is easily solved numerically for the conditional concentration Q_{NO}. For clarity, it can be written in the following form:

$$\frac{\partial \phi}{\partial x} = -A\phi(\phi + B) + E\frac{\partial^2 \phi}{\partial \eta^2}$$

where ϕ is Q_{NO} and *A, B* and *E* are functions of the independent variables, η and x. This equation is parabolic in the x-direction and is discretised using an Euler type scheme as follows:

$$\frac{\phi|_j^{n+1} - \phi|_j^n}{\Delta x} = -A|_j^n \, \phi|_j^n \left(\phi|_j^{n+1} + B|_j\right) + E|_j^n \frac{\phi|_{j+1}^n - (1-r)\phi|_j^n + r\phi|_{j-1}^n}{r(1+r)(\Delta\eta|_j)^2}$$

where the superscripts '*n*' and '*n+1*' denote neighbouring points on the *x*-grid and the subscripts '*j-1*', '*j*' and '*j+1*', neighbouring points on the η-grid. As can be seen, the chemical reaction term (first term on right) is linearised into an implicit and explicit part and the micro-mixing term (last term on right) is handled using central differencing in the η-direction and is explicitly evaluated for marching in the *x*-direction.

Thus Eq. 4 is solved by stepping through in the *x*-direction from imposed initial conditions, with a non-uniform geometric progression discretised grid with expansion factor *r*=1.07 in the η-direction (from η = 0 to 1) and with a 200 x 3000 (η-*x*) grid. The above semi-implicit treatment of the chemical reaction term greatly improves numerical stability compared with a purely explicit approach, so that practical step sizes for the plume can be employed. The computer program runs in about 4 seconds on a 200 MHz PC and is accurate and stable with the above grid spacing applied over a distance of 80 plume heights in the x-direction.

2.3. Probability Density Function

The pdf of $\hat{C}$, $P(\hat{C})$, is a convenient way to quantify the state of mixing of the conserved scalar in dispersion modelling. Recently Yee & Chan (1997) presented a parameterised concentration pdf, suitable for surface point sources under a range of commonly encountered atmospheric conditions. The only inputs required to specify the pdf are the first two moments of the conserved scalar. As these were not measured in the atmospheric experiments, we have estimated them, as specified in section 4.

The pdf of Yee & Chan (1997) takes the form of a clipped-gamma pdf viz.

$$P\left(\frac{\hat{C}}{\overline{\hat{C}}}\right)=\left(\frac{1}{s}\left(\frac{\hat{C}}{\overline{\hat{C}}}+\lambda\right)\right)^{k-1}\frac{1}{s\Gamma(k)}\exp\left(-\frac{1}{s}\left(\frac{\hat{C}}{\overline{\hat{C}}}+\lambda\right)\right)+(1-\gamma)\delta\left(\frac{\hat{C}}{\overline{\hat{C}}}\right),$$

where Γ(k) denotes the Gamma function, δ is the Dirac delta function, and γ is the scalar intermittency, which is the probability of plume fluid being present at a given location. Yee & Chan (1997) have used field data to find empirically a functional relation for γ as

$$\gamma=\gamma(k,s,\lambda)=\frac{\Gamma(k;\lambda/s)}{\Gamma(k)}\approx 3\left(\overline{\left(\frac{\hat{C}}{\overline{\hat{C}}}\right)^2}\right)^{-1}, \qquad (7)$$

where $\Gamma(\upsilon;x)$ denotes the incomplete Gamma function, and *k*, *s* and λ are parameters determined by the solution of three non-linear equations. For convenience, they are determined here by the use of a look-up table as a function of the mean square of the conserved scalar normalised by the square of the mean of the conserved scalar. This is awkward for our present purposes because we prefer to use the fluctuation intensity, $i=\sigma_c/\overline{\hat{C}}$, where σ_c is the root-mean-square (rms) of $\hat{C}$. Conversion to the form required in the look-up table is by use of the equation

$$\overline{\left(\frac{\hat{C}}{\overline{\hat{C}}}\right)^2}=\left(\frac{\sigma_c}{\overline{\hat{C}}}\right)^2+1.$$

Their method gives the pdf at any point of interest downstream of a point source under convective, neutral and stratified conditions. The only required inputs are the conserved scalar mean, $\overline{\hat{C}}$, and the conserved scalar rms, σ_c, at the point of interest. It should be noted, however, that σ_c cannot easily be predicted by current dispersion models and careful judgment is

required in its selection. Fortunately, the sensitivity of the CMC model to the choice of σ_c is relatively low, as discussed below.

Examples of the pdf on the centreline at two downstream locations are shown in Figure 1. Three intensities of fluctuation are shown covering the expected range for this type of plume in the atmosphere. The Dirac delta function associated with the intermittency at $\hat{C}/\hat{C}_s = 0$ is omitted for clarity and its area (1 - γ) is shown in the legend on the Figure. Each pdf is normalised so that the total area including the Dirac delta function is unity. So, in summary, use of the Yee & Chan (1997) pdf in this model requires the specification of both the mean and the variance (or r.m.s.) of the conserved scalar.

3. Field Data

We use the field campaign of Janssen *et al*. (1990), who made airborne measurements of plumes released from power station chimneys in Holland. Their data have been used by others including Vila *et al*. (1990) to investigate the effect of turbulence on chemical reaction in the atmosphere. In this paper, we restrict attention to one set of measurements shown as case 2 in Figure 5 of Vila *et al*. (1990), which is a winter daytime measurement. Under such conditions it is assumed the back reaction to create O_3 from NO_2 is negligible. The emissions and meteorological conditions are listed in Table 1.

Table 1. Emissions and meteorological conditions for the reactive plume from Janssen *et al.* (1990).

Initial Concentration of NO	S_{NO}	877 ppm
Emission of NO		0.2 kg s^{-1}
Flow Rate		100 m^3 s^{-1}
S_{NO} / S_{NO_x}		90%
Stability Class (Pasquill)	D	
Effective Plume Height	H	215 m
Wind Speed at Plume Height	$\overline{U}$	10 m s^{-1}
Ambient Ozone	S_{O_3}	15 ppb
Reaction Rate Constant	k	0.37 ppm^{-1} s^{-1}

Table 2. Plume dispersion characteristics (σ_y and σ_z are shown for general information and are not required by the model) from Janssen *et al.* (1990).

x/H	$\overline{\hat{C}}^*$	$\sigma_y{}^*$ (m)	$\sigma_z{}^*$ (m)
5.0	3.44×10^{-4}	114	40.3
16.3	4.80×10^{-5}	336	98.8
25.0	2.34×10^{-5}	496	137
41.1	1.02×10^{-5}	780	200
60.0	5.43×10^{-6}	1100	266
76.7	3.60×10^{-6}	1377	321

* Estimates obtained from a standard reflected Gaussian plume dispersion model with Pasquill dispersion parameters, given by Janssen *et al*. (1990).

4. Results

To obtain the conditional reactive scalar means, Q_{NO}, Q_{O_3} and Q_{NO_2}, it is necessary to solve the CMC equation (4). The model for the dissipation (micro-mixing) term in this equation is given in equation (6) and an appropriate value of the parameter α must be selected. As a check on the order of magnitude of α, we make rough estimates of the terms in Equation (6) as follows : $\chi \approx \overline{\hat{C}}^2 \overline{U} / x$ and $\eta \approx \overline{\hat{C}}$. The fluctuation intensity is of order unity, which

gives $\alpha \approx \hat{\overline{C}}\overline{U}/x$. Substituting values at *x/H* = 41.1 from Table 2 gives $\alpha \cong 1\text{x}10^{-8}$ s^{-1}. Values of Q_{NO}, Q_{O_3} and Q_{NO_2} are shown in Figures 2 (a), (b) and (c), and were obtained from CMC calculations using the linear model for the conditional scalar dissipation with the parameter α being varied through four values from $\alpha = 0$ to $8\text{x}10^{-7}$ s^{-1} in order to cover the expected range. It is not possible to select the most appropriate value of α from the conditional concentrations shown in Figure 2 because there are no equivalent field data. Selection of α will be done using the mean NO_2 field data, see below.

The case of $\alpha = 0$ s^{-1} is the RDL and is shown on the Figure with symbols on the lines for emphasis. It represents a maximum limit on the extent of reaction and so forms a lower bound on Q_{NO} and Q_{O_3} and an upper bound on Q_{NO_2}. Also shown in Figure 2 is the equilibrium limit (for details see Brown & Bilger, 1998), which represents instantaneous chemical reaction ($k \to \infty$). This is a more conservative maximum limit on the extent of reaction than the reaction dominated limit, which represents instantaneous mixing but realistic values of *k* for the time of convection. The case of mixing without chemical reaction ($k \to 0$) is the frozen limit giving $Q_{NO_2} = 0$ because NO_2 is a chemical product. Unfortunately no conditional reactive scalar means were measured in the field data of Janssen *et al.* (1990) so it is not possible to compare the model results directly. However, presenting the data in this way is useful because it is shows clearly the relative positions of the frozen, equilibrium and reaction dominated limits. Laboratory measurements of conditional reactive scalar means are available (Bilger *et al.*, 1991 and Brown & Bilger, 1998 among others) and it is hoped that field data will be measured in the near future. Such measurements would be of great value for studying the effects of atmospheric turbulence on chemical reaction and in the development of improved models.

Mean NO_2 concentration, $\overline{C}_{NO_2}$, produced by chemical reaction is shown as a fraction of local $\overline{C}_{NO_x}$ in Figure 3. Model predictions were obtained by weighting Q_{NO_2} from Figure 2 (c) with the pdf from Figure 1 and integrating through the range of η according to equation (5). The values at each x-position for the conserved scalar mean used in defining the pdf were interpolated from those given in Table 2 and S_{NO} was taken to be the value given in Table 1. Sensitivity of $\overline{C}_{NO_2}$ to the variation in conditional scalar dissipation, $\langle\chi|\eta\rangle$, is shown for four values of α used above. The best fit to the data is given by $\alpha = 3\text{x}10^{-7}$ s^{-1}, which is close to the

order of magnitude estimate of α given above. At any given downstream location the pdf is sensitive to variation in the intensity of fluctuation, *i,* as shown in Figure 1. However, it was found that $\overline{C}_{NO_2}$ was relatively insensitive to the pdf used for weighting Q_{NO_2}. The variation in $\overline{C}_{NO_2}$ at any *x/H* due to change in *i* from 1.5 to 2.0 (not shown) was found to be less than 10%. Therefore, the Figure only shows $\overline{C}_{NO_2}$ calculated using a pdf with *i* = 1.75. The sensitivity of $\overline{C}_{NO_2}$ to change in the conditional scalar dissipation is significant, showing that it is critical to model this correctly for realistic results to be obtained from the CMC model.

The equilibrium and reaction dominated limits are simple approximations for predicting $\overline{C}_{NO_2}$, however they cannot be calculated without knowledge of the conserved scalar pdf. Two other simple assumptions for predicting $\overline{C}_{NO_2}$, which do not require knowledge of the pdf, are: (i) all NO emitted at the stack is instantaneously converted to NO_2, and (ii) ambient O_3, S_{O3}, is a ceiling on NO_2, which inherently assumes that all mixing between plume and ambient air takes place at the point of release (Cole & Summerhays, 1979). When applied to the present simplified application (where all emissions from the stack are taken as NO) the concentration of $\overline{C}_{NO_2}$ is

$\overline{C}_{NO_2} = S_{O_3}$ when $\overline{C}_{NO_X} > S_{O_3}$ and

$\overline{C}_{NO_2} = \overline{C}_{NO_X}$ when $\overline{C}_{NO_X} \le S_{O_3}$.

The first assumption gives a value of $\overline{C}_{NO_2} / C_{NO_X} = 1$ at all *x/H,* which, from Figure 3, grossly over-estimates the conversion of NO to NO_2 by a factor of 10 close to the stack (*x/H* = 16.3), and by a factor of 2 (for $\alpha = 3\text{x}10^{-7}$ s^{-1}) further downstream (*x/H* = 76.8). The second assumption is not much better, giving values of $\overline{C}_{NO_2} / C_{NO_x}$ = 0 for *x/H* = 0 rising quickly to $\overline{C}_{NO_2} / C_{NO_x}$ = 1 for *x/H* ≥ 30.

A limited data set of three points from Janssen *et al*. (1990) is also shown in Figure 3. The general trend of the CMC predictions and RDL to increase with *x/H* is similar to that of the field data. Even though the comparison with only three points is not conclusive, it gives confidence in extending the modelling approach to other field data.

5. Summary

From the limited comparison above it can be seen that the model results for calculating mean NO_2 concentrations follow similar trends to that of field data. With the appropriate choice of a model parameter the results agree well with the field data. This confirms the usefulness of this modelling methodology of combining the conditional moment closure with an atmospheric scalar probability density function. The simplified form of the model, the reaction dominated limit, is found to form a limiting maximum concentration of NO_2 that is less conservative than other approaches. While the present model maintains consistency between the form for the conditional scalar dissipation (needed for CMC) and the pdf, the choice of the appropriate model parameter is not clear. Motivated by this need, Brown & Sawford (2000) have developed an improved modelling method that maintains consistency and provides a more rational basis for selecting the model parameter.

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Figures

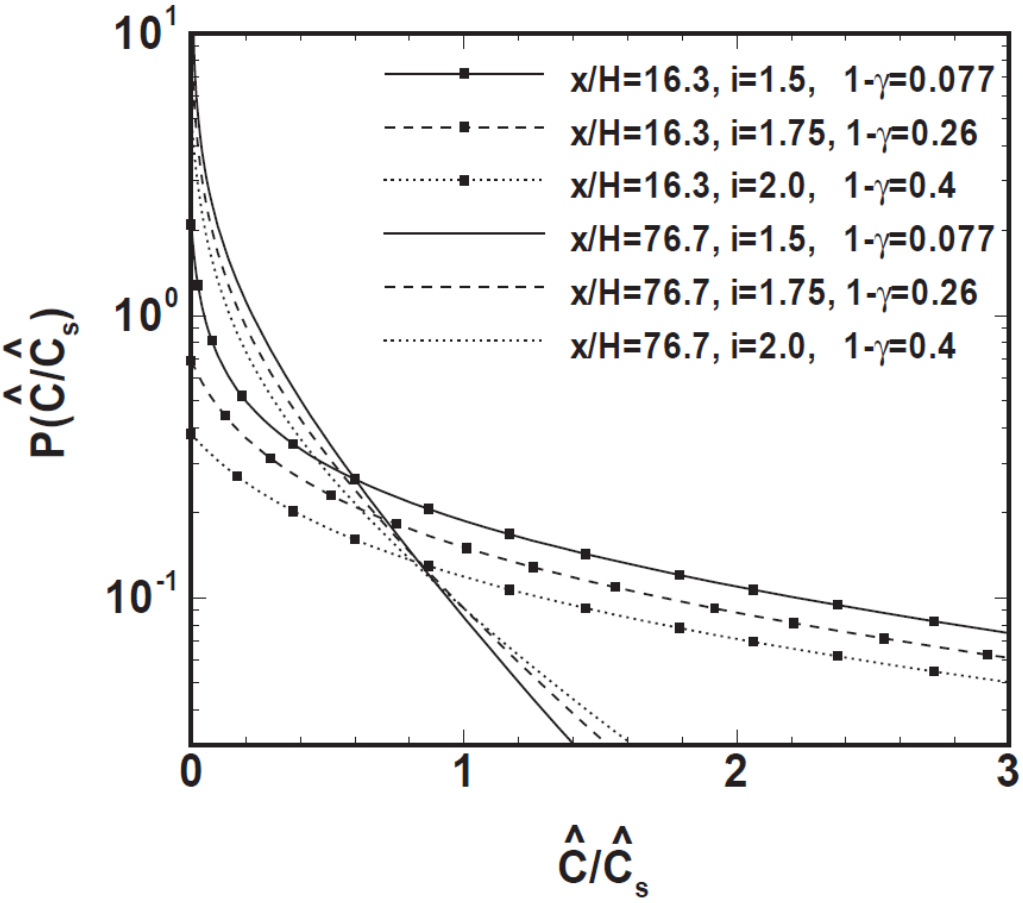

Figure 1. PDF of $\hat{C}$ at two downstream locations and three intensities of fluctuation as shown in the legend.

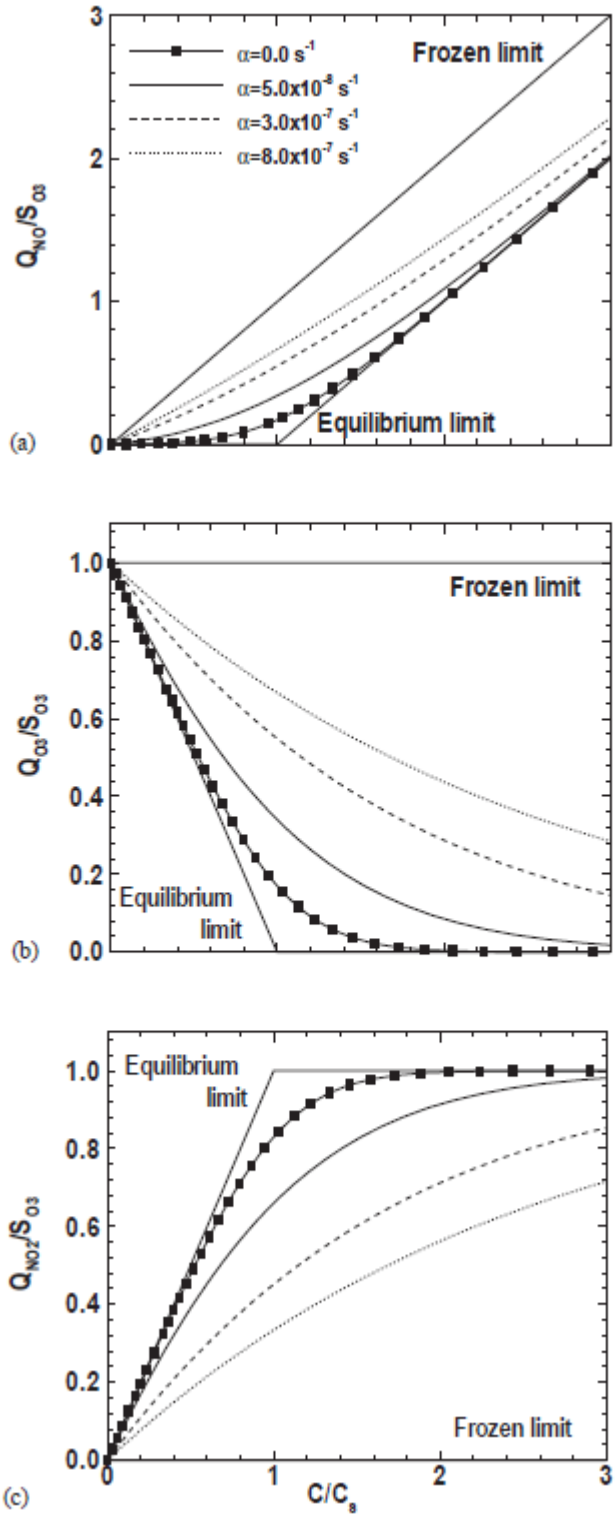

Figure 2. Model predictions for conditional reactive mean concentrations, Q_i, at the downstream location x/H = 41.1: (a), Q_{NO}; (b), Q_{O_3}; (c), Q_{NO_2}. Sensitivity of Q_i to variation in the linear model for the conditional scalar dissipation, $\langle\chi|\eta\rangle = \alpha\eta$, is shown for four values of α. The case of $\alpha = 0\ s^{-1}$ is the reaction dominated limit. Frozen and equilibrium limits are also shown.

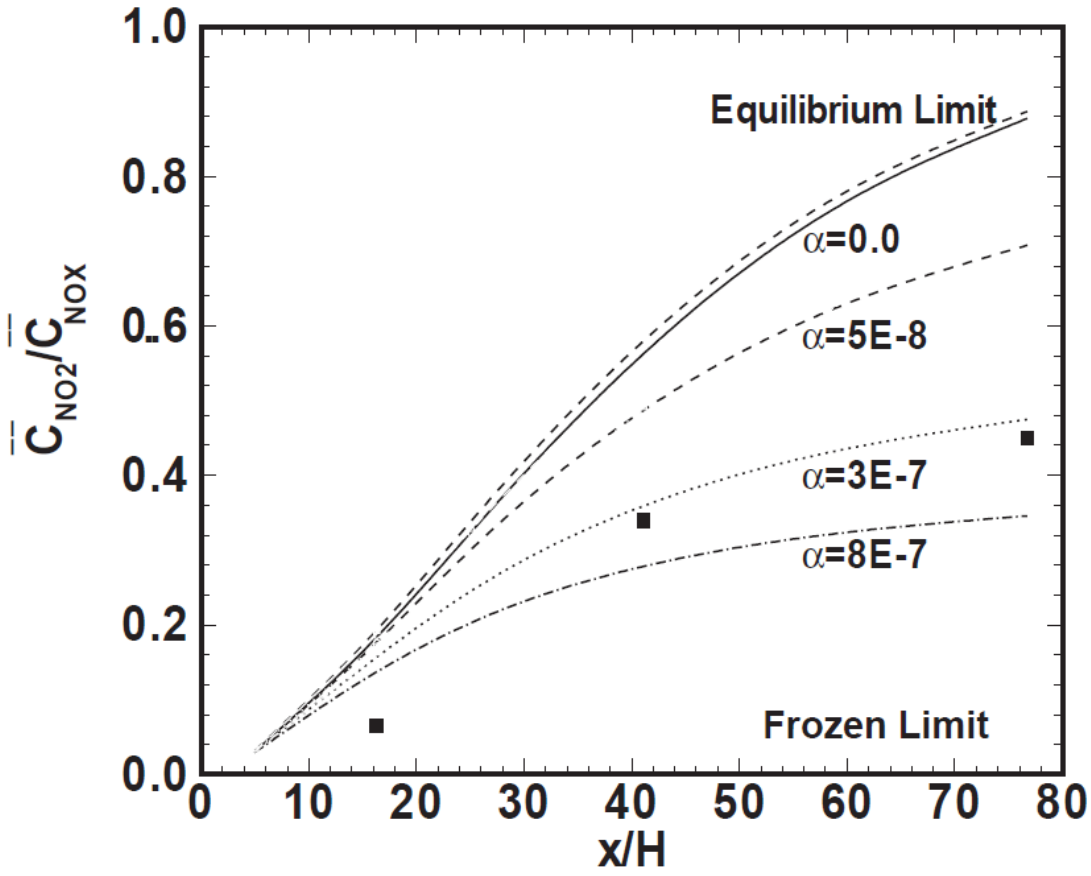

Figure 3. Mean NO_2, produced by chemical reaction shown as a fraction of local $\overline{C}_{NO_x}$, $\overline{C}_{NO_2}/\overline{C}_{NO_x}$. Field data of Janssen *et al*. (1990) represented by full squares. RDL (for which α = 0 s^{-1}) and CMC predictions for various α shown on the Figure. The equilibrium and frozen limits (solid lines) are also shown.